Supporting Information

Enhanced d-π overlap in graphene supported Ni/PtNi heterojuncction for efficient seawater hydrogen evolution

*Xiong Yang,[‡a] Yu-Xuan Xiao,[‡b] Xue-Qi Zhang,[‡a] Fei Yu,[a] Ge Tian,[*a] Wen-Ying Zhao,[a] Ling Shen,[a] Song Zhang,[a] Xiao-Yu Yang,[*a]*

[a]*State Key Laboratory of Advanced Technology for Materials Synthesis and Processing &International School of Materials Science and Engineering & Shenzhen Research Institute & Joint Laboratory for Marine Advanced Materials in National Laboratory for Marine Science and Technology (Qingdao), Wuhan University of Technology, Wuhan, 430070, China.*

[b]*School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai, 519082, China.*

* To whom correspondence should be addressed.
Email: xyyang@whut.edu.cn

Experimental section

1. Materials

$Ni(acac)_2$, $Pt(acac)_2$, graphene, oeylamine and oleic acid were purchased from Shanghai Aladdin Biochemical Polytron Technologies Inc. Ethanol, hexane, formaldehyde solution, KOH and NaCl were purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial Pt/C (20 at.% Pt) was purchased from Johnson Matthey Corp. Commercial carbon black (Vulcan-XC 72R) was purchased from Shanghai Cabot Co., Ltd. All chemical reagents were used as received without further purification. De-ionized (DI) water (18.2 MΩcm) was used throughout.

2. Synthesis of Ni/PtNi and Ni/PtNi-G_{1-3}.

In a typical synthesis, 31.4 mg (0.3 mmol) of $Ni(acac)_2$ 48 mg (0.1 mmol) of $Pt(acac)_2$ and 60 mg graphene were first dissolved in 45 mL of oleylamine and 5 mL of oleic acid in a Teflon-lined stainless-steel autoclave with a capacity of 100 mL. After that, 4 ml of formaldehyde solution was injected into the solution and stirred for 15 min until the mixture became homogeneous. Then, the autoclave was kept at 190 ℃ for 12 h. After cooling to room temperature under ambient conditions, the product was collected by centrifugation (10,000 r.p.m. for 10 min) and washed several times with hexane and ethanol to remove impurities.

The control sample of Ni/PtNi, Ni/PtNi-G_1 and Ni/PtNi-G_3 were synthesized by the same methods as for Ni/PtNi-G_3, except for the change in content of graphene from 60 mg to 0 mg, 30 mg and 90 mg, respectively.

3. Physical characterization

Transmission electron microscopy (TEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were conducted with a Talos F200S (Thermo Fisher, USA) in Wuhan University of Technology. X-ray diffraction (XRD) measurements were performed on a Bruker D8-Advance X-ray diffractometer operating with Cu Kα radiation (λ=1.54056 Å). The X-ray photoelectron spectroscopy (XPS) measurements were carried out by an ESCALAB 250Xi (Thermo Fisher, USA). Electron spin resonance (ESR) measurements were performed at the X-band using a JEOL FA 2000 spectrometer. The content analyses of Pt and Ni were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy 7, LEEMAN

LABS INC, USA). Raman spectra of the catalysts were recorded using a single monochromator Renishaw in Via Raman Microscope System 1000 spectrometer equipped with a 100 mW laser with emission at 532 nm equipped with a thermoelectrically cooled CCD detector and a holographic super-Notch filter.

6. Electrochemical measurements

The electrochemical measurements were performed at room temperature using an Autolab working station (Metrohm, Switzerland) with a glassy carbon working electrode. Before measurements, the catalyst dispersion or ink was prepared by mixing certain amounts of catalysts in 880 μL of isopropanol, 100 μL of water and 20 μL of 5 wt.% Nafion solution followed by ultrasonication for 30 min. The Pt loading of all samples on glassy carbon was 3 μg. An Ag/AgCl electrode and a graphite rod (99.99%) were used as the reference and the counter electrodes.

Polarization curves were collected at a rotation rate of 1600 rpm with a sweep rate of 5 mV s^{-1}. And chronopotentiometric measurements were performed in alkaline seawater at 10 mA/cm^2 for 10 h. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 100 kHz to 0.1 Hz with an AC amplitude of 10 mV. All the potentials are presented with reference to the RHE without insulation resistance (iR) compensation.

The catalysts' turnover frequency (TOF) was calculated according to following formula.

$$TOF = \frac{j(\eta)\cdot A\cdot \frac{N_A}{n\cdot F}}{S}$$

Where j(η) is the current density (A cm^{-2} electrode) at an overpotential of η (70 mV); A is the superficial electrode area (0.196 cm^2); N_A is the Avogadro's number, 6.02×10^{23} (mol^{-1}); n is the number of electrons transferred per molecule, 2 for HER; F is the Faraday constant, 96485 (C mol^{-1} electrons); S is the number of active sites. To avoid calculation difficulties, all the metal atoms in the catalysts were assumed as being active sites, which can be determined according to ICP-AES results. As a consequence, only the lowest TOF values for different catalysts were calculated and compared in this work.

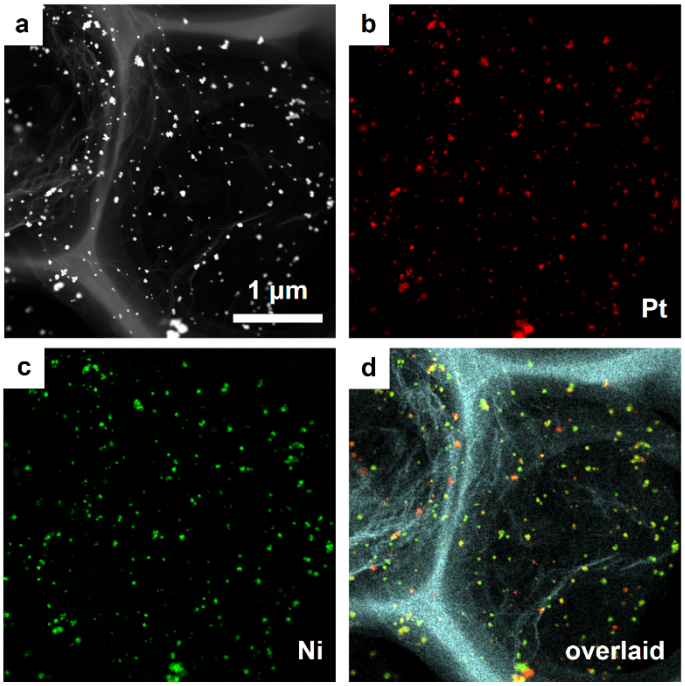

Figure S1. (a) HAADF-STEM image and EDX elemental mapping profiles of (b) Pt, (c) Ni and (d) overlaid color mapping for Ni/PtNi-G.

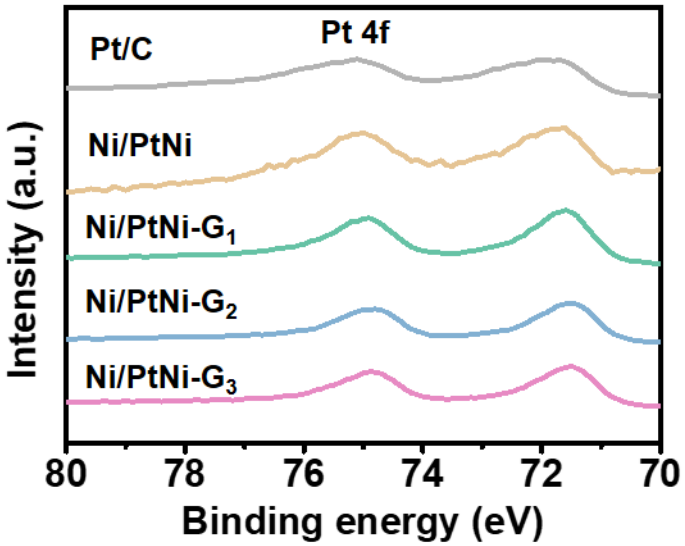

Figure S2. XPS spectra showing the binding energies of Pt 4f signals of Ni/PtNi and Ni/PtNi-$G_{1\text{-}3}$.

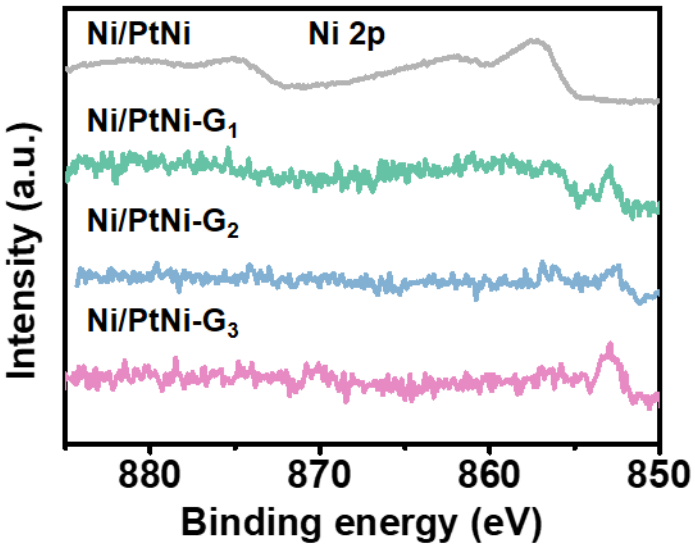

Figure S3. XPS spectra showing the binding energies of Ni 2p signals of Ni/PtNi and Ni/PtNi-$G_{1\text{-}3}$.

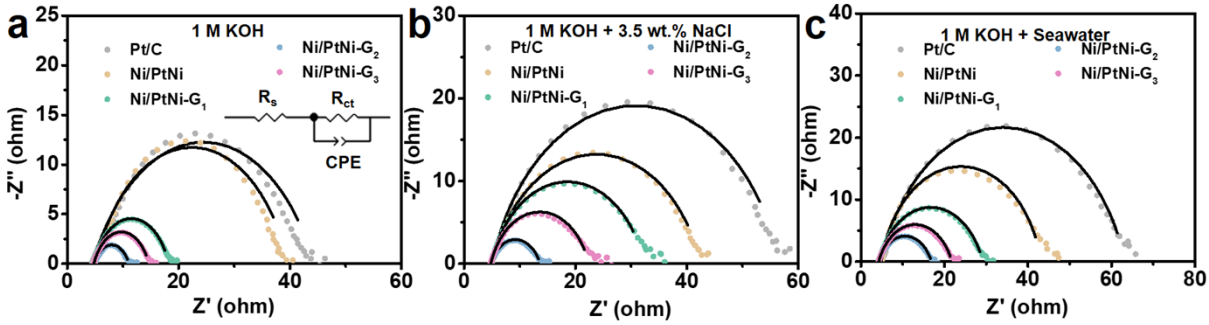

Figure S4. Nyquist plots and analog circuit of commercial Pt/C, Ni/PtNi and Ni/PtNi-$G_{1\text{-}3}$ in alkaline media, alkaline simulated seawater and alkaline natural seawater.

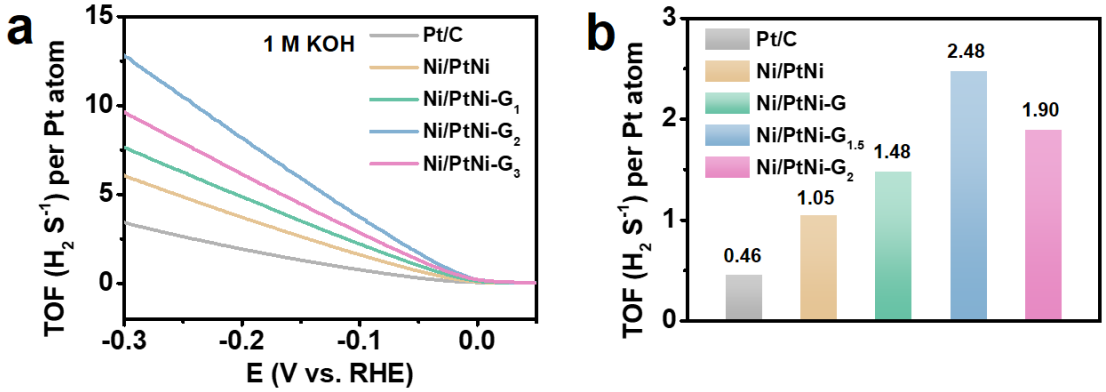

Figure S5. (a) Calculated TOF curves and (b) TOF values at 0.07 V of commercial Pt/C, Ni/PtNi and Ni/PtNi-$G_{1\text{-}3}$ in alkaline media.

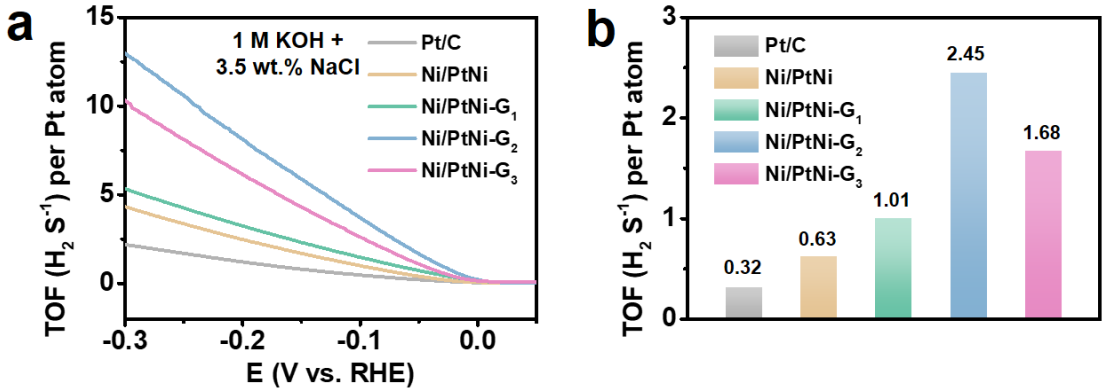

Figure S6. (a) Calculated TOF curves and (b) TOF values at 0.07 V of commercial Pt/C, Ni/PtNi and Ni/PtNi-G_{1-3} in alkaline simulated seawater.

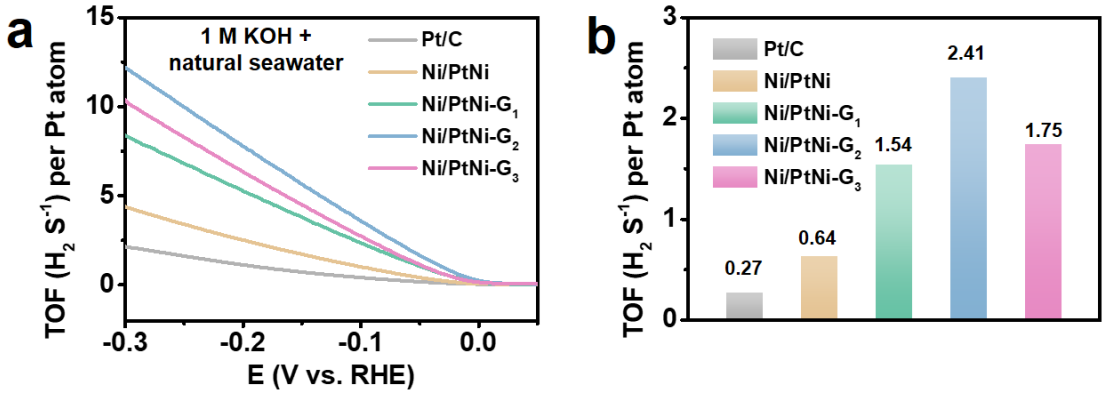

Figure S7. (a) Calculated TOF curves and (b) TOF values at 0.07 V of commercial Pt/C, Ni/PtNi and Ni/PtNi-G_{1-3} in alkaline natural seawater.

Table S1. ICP-AES data showing the Pt: Ni molar ratios of Ni/PtNi and Ni/PtNi-G.

Sample	Pt (at.%)	Ni (at.%)
Ni/PtNi	59	41
Ni/PtNi-G_1	45	55
Ni/PtNi-G_2	48	52
Ni/PtNi-G_3	55	45

Table S2. Peak fitting results of Pt 4f and Ni 2p signals for Ni/PtNi and Ni/PtNi-G_{1-3}.

Sample	B.E. of Pt $4f_{7/2}$ (eV)	B.E. of Pt $4f_{5/2}$ (eV)	B.E. of Ni $2p_{3/2}$ (eV)	B.E. of Ni $2p_{1/2}$ (eV)
commercial Pt/C	72.0	75.3	N.A.	N.A.
Ni/PtNi	71.8	75.1	857.4	875.2
Ni/PtNi-G_1	71.6	75.0	857.1	875.1
Ni/PtNi-G_2	71.5	74.8	856.4	874.2
Ni/PtNi-G_3	71.5	74.8	856.1	873.2

N.A. = not applicable

Table S3. Electrochemical test results of commercial Pt/C, Ni/PtNi and Ni/PtNi-G_{1-3}.

Electrolyte	Sample	Mass Activity ($mA/\mu g_{Pt}$, @70mV)	Overpotential at 10 mA/cm^2 (η_{10}, mV)	TOF (S^{-1})	Tafel ($mV\ dec^{-1}$)
1 M KOH	commercial Pt/C	0.48	89	0.46	60
	Ni/PtNi	1.03	48	1.05	40
	Ni/PtNi-G_1	1.46	34	1.48	34
	Ni/PtNi-G_2	2.46	19	2.48	28
	Ni/PtNi-G_3	1.89	26	1.90	37
1 M KOH + 3.5 wt.% NaCl	commercial Pt/C	0.32	129	0.32	78
	Ni/PtNi	0.63	73	0.63	56
	Ni/PtNi-G_1	1.01	45	1.01	53
	Ni/PtNi-G_2	2.42	21	2.45	28
	Ni/PtNi-G_3	1.66	33	1.68	38
Seawater	commercial Pt/C	0.26	144	0.27	80
	Ni/PtNi	0.64	72	0.64	53

Ni/PtNi-G_1	1.53	33	1.54	38
Ni/PtNi-G_2	2.41	20	2.41	32
Ni/PtNi-G_3	1.73	33	1.75	36

Table S4. Performance of Ni/PtNi-G_2 in comparison to reported catalysts for the HER in alkaline seawater.

Catalyst	Electrolytes	Overpotential (mV@10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Reference
Ni/PtNi-G_2	1 M KOH + 0.5 M NaCl	21	28	This work
	1 M KOH + seawater	20	32	
Ni-SN@C	1 M KOH + seawater	23	41	Adv. Mater. 2021, 33, 2007508
Ni_5P_4@$Ni^{2+\delta}O_\delta(OH)_{2-\delta}$	natural seawater	144	108	Appl. Catal., B 2019, 251, 181
NiCoN|NixP| NiCoN	natural seawater	165	138.2	ACS Energy Lett. 2020, 5, 2681.
MIL-(IrNiFe)@NF	1 M KOH + 0.5 M NaCl	~30	57	J. Mater. Chem. A 2021, 9, 27424-27433
cRu-Ni3N/NF	natural seawater	36	26.1	10.1002/EEM2.12318
l-Rh	1 M KOH + seawater	38	39	Appl. Catal. B-Environ. 2022, 310, 121338
Pt-Co_3O_4/CP	1 M NaOH + 3.5at.% NaCl	47	69	J. Mater. Chem. A 2021, 9, 6316-6324
CNC-MO	1 M KOH + 0.5 M NaCl	~50	78	Nano Energy 2021, 87, 106160
Pt–Co_3O_4/CP	mimic alkaline	54	65	J. Mater. Chem. A, 2021, 9, 6316
C-Co_2P	1 M KOH+ 0.5 M NaCl	58	45.1	Adv. Funct. Mater. 2021, 2107333
CoRuPO/NF	1 M KOH + seawater	62	97	RSC Adv. 2020, 10, 27235
NiRuIr/G	natural seawater	~80	48	Electrochemistry Communications 111 (2020) 106647
Cu@Co-CoO/Rh	1 M KOH + 0.5 M NaCl	137.7	124.8	Small 2021, 17, 2103826
Ni-SA/NC	1 M KOH + seawater	139	123	Adv. Mater. 2020, 33, 2003846
Pt–Ru–Mo	natural seawater	196	99.8	J. Mater. Chem. A, 2016, 4, 6513
Pt–Ru–Ni		206	103.5	
Pt–Ru–Co		222	109.5	
Pt–Ru–Fe		248	122.3	
Pt–Ru–Cr		256	125.8	